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(54) MANUFACTURE OF ARTICLE CONTAINING CARBON NANOTUBE AND DEVICE INCLUDING CUT-OFF CARBON NANOTUBE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for improving emission characteristics of a set of aligned nanotubes.
SOLUTION: Emission characteristics of aligned nanotube array 12 are improved by cutting off an end of a nanotube. The nanotube 12 which has a length of not more than 30% of an average cut-off nanotube and has an end substantially without an end cap is provided by cutting off the end. The end without the cap provides a desired electric field convergence, and high uniformity increases the number of contributing nanotubes.

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CLAIMS

[Claim(s)]
[Claim 1] The approach for manufacturing the object containing the carbon nanotube characterized by having the step which offers the array of the carbon nanotube which aligned, and the step which cuts off said some of nanotubes [at least] so that there may be no end cap in at least 10% of the nanotube cut off.
[Claim 2] The approach according to claim 1 characterized by there being

no end cap in said at least 50% of cut-off nanotube.
[Claim 3] It is the approach according to claim 1 which said cut-off nanotube has less than 30% of height of criteria distance, and is characterized by said criteria distance being the smaller one of the mean distances between the nanotubes which adjoin the average height of the cut-off nanotube.
[Claim 4] The approach according to claim 1 that said cut-off nanotube is characterized by having less than 30% of height of the average height of said cut-off nanotube.
[Claim 5] The approach according to claim 1 characterized by said step to cut off containing the step which turns a high energy beam to a nanotube.
[Claim 6] Said high energy beam is an approach according to claim 5 characterized by being chosen from a laser beam, an electron beam, and an ion beam.
[Claim 7] The approach according to claim 1 that said step to cut off is characterized by including the step which gives a temperature gradient to said nanotube in the ambient atmosphere containing oxygen so that said some of nanotubes may stop burning.
[Claim 8] Said temperature gradient is an approach according to claim 7 characterized by being given by making the body which had the nanotube heated contact.
[Claim 9] Said heated body is an approach according to claim 8 characterized by including the heated cutting edge.
[Claim 10] Said cutting edge is an approach according to claim 9 characterized by being heated by at least 400 degrees C.
[Claim 11] Said step to cut off is an approach according to claim 1 characterized by including the step in which carbon is dissolved from a nanotube edge by making a carbon fusibility ingredient contact.
[Claim 12] Said carbon fusibility ingredient is an approach according to claim 11 characterized by including a rare earth metal and a non-rare earth metal.
[Claim 13] Said carbon fusibility ingredient is an approach according to claim 12 characterized by including at least one of Ce, La, Fe, and Mn.
[Claim 14] It is the approach according to claim 11 which said carbon fusibility ingredient is dissolving and is characterized by placing said nanotube edge into a dissolution ingredient.
[Claim 15] It is the approach according to claim 11 characterized by for said carbon fusibility ingredient being a solid-state, and rubbing a nanotube edge against said solid material.
[Claim 16] Said step to cut off is an approach according to claim 1

characterized by to include the step to which a nanotube is exposed according to at least one process chosen from the step which grinds the step which puts said nanotube into a capsule in a solid-state matrix, the step from which said matrix is cut, and said matrix, and the step which carries out etching removal of the matrix ingredient from said exposed nanotube in order to offer an ejection nanotube.
[Claim 17] Said cut-off nanotube is a device characterized by having less than 30% of height of the nanotube height from which the average was cut out in the device containing the cut-off carbon nanotube, and there being no end cap in said at least 10% of cut-off nanotube.
[Claim 18] Said cut-off nanotube is a device according to claim 17 characterized by having less than 10% of height of the nanotube height from which the average was cut out.
[Claim 19] Said cut-off nanotube is a device according to claim 17 characterized by having 0.01 thru/or average height of 1000 micrometers from the front face of a support substrate.
[Claim 20] Said cut-off nanotube is a device according to claim 19 characterized by having 0.1 thru/or average height of 100 micrometers from the front face of said support substrate.
[Claim 21] Said device is a device according to claim 17 characterized by being a storage-of-energy device.
[Claim 22] The device according to claim 17 characterized by there being no end cap in said at least 50% of cut-off nanotube.
[Claim 23] It is the device which said cut-off nanotube has less than 30% of height of criteria distance in the device containing the cut-off carbon nanotube, and said criteria distance is the smaller one of the mean distances between the nanotubes which adjoin the average height of the cut-off nanotube, and is characterized by there being no end cap in said at least 10% of cut-off nanotube.
[Claim 24] Said cut-off nanotube is a device according to claim 23 characterized by having less than 10% of height of said criteria distance.
[Claim 25] Said cut-off nanotube is a device according to claim 23 characterized by having 0.01 thru/or average height of 1000 micrometers from the front face of a support substrate.
[Claim 26] Said cut-off nanotube is a device according to claim 25 characterized by having 0.1 thru/or average height of 100 micrometers from the front face of a support substrate.
[Claim 27] Said device is a device according to claim 23 characterized by being a storage-of-energy device.
[Claim 28] The device according to claim 23 characterized by there being

no end cap in said at least 50% of cut-off nanotube.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the field emitter which is applied to the device containing an electron field (electronic electric field) emitter, especially contains a carbon nanotube.
[0002]
[Description of the Prior Art] The electron field emitter is useful for various applications including a microwave amplifier and a flat panel field emission display.
[0003] A microwave vacuum-pipe device like power amplifier is the indispensable component of the microwave system of many present age containing a communication link, a radar, electronic war, and a navigation system. Although a semi-conductor microwave amplifier is available, generally they lack the capacity of the power needed by almost all the microwave system. A microwave tube amplifier offers the microwave energy in power level high for whether your being Haruka by contrast. The higher power level of a tubing device is as a result of the fact of going on at a rate high for whether your being Haruka in a vacuum rather than an electron can set to a semi-conductor. A high-speed thing enables use of bigger structure by the same transit time. And big structure makes bigger power level possible.
[0004] Typically, a microwave tube device operates introducing an electron beam all over the field where a beam interacts with an input signal, and by pulling out an output signal from the modulated electron beam. For example, A.W.Scott, Understanding Microwaves, Ch.12, and John Wiley & Sons (1993) Refer to. A microwave tube device contains the traveling wave tube, grid tubing, a klystron, a crossover field form amplifier, and a gyrotron.
[0005] The usual source of the electron for the microwave tube is a thermion radiation cathode (cathode), and is formed from the tungsten cathode by which the coat was typically carried out arbitrarily with mixture with a barium oxide or a thorium oxide. A cathode is heated to the temperature of about 1000 degrees C, in order to generate thermion electron emission to several A [per square centimeter] order.

[0006] Required heating of a thermion cathode produces many problems. Since a cathode, therefore tubing stop already working when the main components of a cathode like barium oxide evaporate a cathode life in a high operating temperature and barium is lost, a cathode life is restricted. Many traveling wave tubes (TWT) have a life of operation also for example, with short 1 old person.

[0007] Moreover, the need of making a cathode even into operating temperature produces radiation delay in several minutes, and this cannot be accepted in most commercial applications. Furthermore, generally, elevated-temperature actuation needs a circumference cooling system like a fan, and, thereby, increases the size of a device or the whole system. Therefore, to develop the microwave tube device which does not need such elevated-temperature actuation, for example, a cold cathode device, is desired.

[0008] The application of another promising field emitter is a flat-panel display in which the thin matrix address is possible. For example Semiconductor International, December 1991, p.46, and C.A.Spindt etc. -- it depends IEEE Transactions on Electron Devices, Vol.38, and 2355 (1991) -- I.Brodie It reaches. C.A.Spindt It depends. Advancesin Electronics and Electron Physics, P. W.Hawkes Editing, Vol.83, and pp.1 (1992), It reaches. J.A.Costellano It depends. Handbook of Display Technology, Academic Press, and 254 (1992), And refer to U.S. Pat. No. 4,940,916, No. 5,129,850, No. 5,138,237, and No. 5,283,500.

[0009] It is known that various properties are advantageous as a cathode ingredient of a field emission device. Electrical-potential-difference actuation is possible for a radiation current at the driver voltage of the range which can be obtained from the integrated circuit obtained immediately to a convenient thing. Generally the cathode emitted by electric field 25v [/micrometer] or less to a typical device dimension (for example, spacing between [of 1 micrometer] gate-cathodes) is desirable for a typical CMOS circuit. Desirably, the range of radiation current density is 2 one to 10 mA/cm to a flat-panel display application, and it is >100mA/cm2 to a microwave power amplifier application.

[0010] The radiation property is desirably [it is reproducible in a certain source and another source desirably, and] stable in the very long time interval of tens of thousands of hours. Since desirably prevents restricting the device engine performance, radiation fluctuation (noise) is fully small. A cathode is tolerant desirably to reduction which is not [in vacuum environments, such as a chemical reaction with an ion bombardment and residual gas, too much temperature, and arcing,] desirable. Finally, manufacture of a cathode can suit the

broad application instead of a very critical process cheaply desirably.
[0011] Typically, the usual field emission cathode ingredient consists of a metal like Mo which has the tip where submicron size sharpened, or a semiconductor material like Si. The control voltage by which it is needed for radiation although the useful radiation property has been shown about these ingredients is comparatively high because of these high work functions and a comparatively blunt (that is, insufficiently sharp) tip (about 100 V).
[0012] This high-voltage actuation increases the instability which gives a damage by the ion bombardment and surface diffusion to the tip of an emitter, and needs the high power flux density which should be supplied from the source of the exterior for making the radiation current density to need. the field where manufacture of a uniform sharp tip is big -- especially -- difficulty -- it is tedious and expensive. Furthermore, a lack [the drag force of the conditions of typical operating environment, for example, ion bombardments, and these ingredients / chemically as opposed to a reaction and a extreme temperature with an activity kind] is a problem.
[0013] The carbon ingredient (a diamond and carbon nanotube) has appeared as a possible useful electron field emitter recently. Technical progress was late a little because of the inclination of graphite-izing in the diamond emitter in the radiation current on which a diamond exceeds about 30 mA/cm2, for example by the negative or low electron affinity on the hydrogen TAMINE Ted (hydrogen-terminaetd) front face although there is an advantage and which increased, and the heterogeneity of radiation.
[0014] A carbon nanotube is characterized by the high aspect ratio (> 1,000) and small tip radius of curvature (- 5 -50 nm). These geometric properties are combination with a mechanical strength and chemical stability with an expensive capillary, and make the carbon nanotube attractive as an electron field emitter. for example, the German patent No. 4,405,768 and Rinzler etc. -- it depends Science, Vol.269, and 1550 (1995) -- DeHeer etc. -- it depends Science, Vol.270, and 1179 (1995) -- Saito etc. -- it depends Jpn.J.Appl.Phys., Vol.37, and L346 (1998) -- Wang etc. -- it depends Appl.Phys.Lett., Vol.70, and 3308 (1997) -- Saito etc. -- it depends Jpn.J.Appl.Phys., Vol.36, and L1340 (1997) -- and -- Wang etc. -- it depends Appl.Phys.Lett., Vol.72, and 2912 (1998) reference -- things.
[Problem(s) to be Solved by the Invention]
[0015] Unluckily, typically, the carbon nanotube is available in the form of fine particles like [again] ** spaghetti like the needle which

is not united with field emitter device structure easily or conveniently. However, in order that a process like chemical vapor deposition may make well the ensemble (one set) of the nanotube which aligned on the substrate, it has been used recently.
[0016] for example, Ren etc. -- it depends Science, Vol.282, 1105 (1998), and Li etc. -- Science to depend, Vol.274, and 1701 (1996) -- and -- deHeer etc. -- it depends Science, Vol.268, and 845 (1995) Refer to. The radiation property of such ensemble of the nanotube which aligned is not optimized, carrying out a deer, but a method of improving the radiation property of the ensemble of such a nanotube that aligned is desired.
[0017]
[Means for Solving the Problem] The method of specifically manufacturing the nanotube ensemble which was discovered recently and which aligned offers the nanotube in which the property which is not desirable as for some is shown. Especially a nanotube edge tends to be capped with the carbon of metal particle (particle) or a comparatively big field, and the nanotube itself shows uneven height. The nanotube by which termination was spherically carried out by the carbon hemisphere which has a diameter below the diameter of the nanotube itself as being capped is not included.
[0018] The capped edge is in the inclination to be opening, for example, to reduce electric-field concentration compared with the spherical edge of the small diameter by which termination was carried out with the folded edge or carbon, and uneven height makes a nanotube with a low high nanotube cover electrically, and decreases the number of the nanotubes which this contributes to radiation. The average difference from perpendicular perfect alignment means that it is smaller than 30 degrees to the back face in the point of the front face which uses for example, a high resolution scanning electron microscope as having aligned, and the nanotube judged projects.
[0019] However, this invention offers the improved emitter structure by cutting off the edge of such nanotube ensemble that aligned. Cutoff offers the nanotube which measures from the front face of a back face and has the homogeneity of less than 30% of height of average nanotube height, and, specifically, offers the nanotube ensemble which does not have at least 10% end cap in at least 50% of nanotube desirably. The cut-off edge which is obtained offers desirable electric-field concentration, and the homogeneity of the height obtained increases the number of the nanotubes to contribute. Cutoff is performed by which suitable technique.
[0020] In 1 operation gestalt, in order that a high energy beam may cut

off the nanotube of the nanotube ensemble which aligned, it is used (drawing 1). By heating alternatively in an oxidizing atmosphere, it is also possible to burn the upper part of a nanotube (drawing 2). A nanotube edge is contacted to the solid-state metal (drawing 3 B) which has the melted carbon dissolution ingredient (drawing 3 A) or high carbon fusibility in alternative. In another operation gestalt, the nanotube which aligned is embedded into a solid-state matrix, is cut or ground, and it is etched in order to offer an ejection nanotube (drawing 4).

[0021] Although the structure acquired maintains the direction of a nanotube which aligned, it shows further the nanotube of the uniform height which has the tip which does not have a useful sharp cap in field emission.

[0022]

[Embodiment of the Invention] nanotube emitter structure and the manufacture approach -- in reliable design and manufacture of a field emitter, high radiation current density is desirable and this can be obtained efficient, powerful, and by increasing the nanotube consistency on an emitter front face. It was comparatively difficult to offer the carbon nanotube of high density on an emitter front face. This is a certain part and is because there is a problem which the nanotube resembles the set of the wire of the needle which generally twined gently [uneven height], or a spaghetti mold, and attaches a nanotube in a conductive substrate in a certain part. The technique discovered recently for forming the nanotube array which aligned enables achievement of such high density more easily, carrying out a deer.

[0023] Furthermore, electronic field emission is strengthened by concentration of the electric field near [sharp] the tip when the geometric description of an emitter is made small. The small diameter of a carbon nanotube, for example, smallness like 1.3nm, offers the effective electric-field concentration description. However, the edge of a nanotube offers small radius of curvature also to the electric-field concentration and electron emission which were strengthened.

[0024] The electron emission from a nanotube tip is actually easier than the radiation from a side face. For example, tip radiation is produced on electric-field level low for whether your being Haruka. Thus, it is advantageous to form the nanotube field emitter structure where many nanotube edges were exposed more. Moreover, it is still more useful to have an edge without the sharp cap turned to the anode of the emitter device offered by this invention.

[0025] The structural description of another, important nanotube field

emitter is the height at the tip of ejection from the front face of a substrate. The homogeneity of ejection is important in order to increase the number of the tips of a nanotube which contribute to radiation. Contribution at a tip which is dominant as for the contribution to field emission, and has not projected it out of near by these highest tips for electric shielding of the local electric field by the concrete highest ejection tip becomes small.

[0026] Therefore, the nanotube cut off about the field emission application has the height within 30% of criteria-distance desirably, and is 10% of within the limits more preferably. The distance of criteria is the smaller one of the mean distances between the nanotubes which adjoin the average height of the nanotube cut out from the substrate front face. The nanotube cut off to applications other than radiation, for example, the application of a storage of energy, has preferably the height of 30% of within the limits of the nanotube height from which the average was cut out, and is 10% of range more preferably.

[0027] For these reasons, this invention offers the structure which shows the emitter consistency and radiation current density which were improved by cutoff of the nanotube array which aligned. The manufacture of emitter structure is as follows.

[0028] The carbon nanotube ensemble which aligned is manufactured, namely, it is obtained. Although the mechanism with exact growth of the nanotube which aligned is not known clearly, the approach for obtaining growth is learned as follows. Such a manufacture approach includes chemical vapor deposition, electric arc discharge, and laser excision. Or it was impressed in the growth plasma in nanotube composition, the growth which aligned by the electric field which exist automatically can be strengthened. It is suitable in order that other techniques like use of a temperature gradient may promote the growth where the nanotube aligned.

[0029] And a nanotube offers the nanotube of the uniform height which has a sharp tip. It is formed on the edge where the carbon semi-sphere of a small diameter was cut off after cutoff. As mentioned above, such a semi-sphere is not considered to be a cap when a diameter is not larger than the diameter of the nanotube itself. an average nanotube diameter -- a nanotube -- a single Wall mold and a multi-wall mold -- or it is in the range of about 1.3 to 200 nm depending on the bundled single Wall mold.

[0030] A single Wall nanotube is in the inclination which shows 1 thru/or the typical diameter of 5nm order, and often becomes the form of a bundle. A multi-wall nanotube is in the inclination which shows 10

thru/or the typical diameter of 50nm order including this cardiac graphite cylinder. The aspect ratios of both types are 100 thru/or 10,000 typically. Typically, the average height from the support substrate of the nanotube by this invention aligned and cut off is in the range of 0.01 to 1000 micrometer, and is in the range of 0.1 to 100 micrometer preferably.

[0031] According to 1 operation gestalt of this invention, it is used in order that the high energy beam 100 may cut off the ensemble of the nanotube 12 which aligned, as shown in drawing 1 . Although a suitable beam contains a laser beam, an electron beam, and an ion beam (for example, an argon or oxygen plasma), it is not limited to these. The ion beam or the plasma beam is advantageous. For example, a discrete source beam, two or more collimated beams, or a flat beam can be used by any in the quiescence mode of illumination, or scanning mode they are.

[0032] Typically, a substrate rotates in order to improve the homogeneity of cutoff. A nanotube 12 is evaporated in the point that a beam contacts, and one nanotube is cut off at a time as a beam spreads through the nanotube which aligned. In order that optical vacuum suction or loose gas spraying may sweep out waste 14, in the case of a laser beam, it is used especially arbitrarily.

[0033] A higher nanotube is in the inclination which absorbs and evaporates the beam which carries out incidence, a thereby more short nanotube is covered, and the inclination of a beam is desirably set so that this shadow effectiveness may be acquired. The range of the factor of 3 of [1 nm/dN] has a desirable inclination, this is measured by the radian, and dN is the mean distance between adjoining nanotubes here. As opposed to the sample which has the low consistency of a nanotube, the demand of the inclination of a beam and the flat demand of a substrate make this operation gestalt comparatively difficult.

[0034] It depends for the desirable level of beam energy on the property of a beam, the size of a nanotube array sample, a consistency, and the mode of beam actuation substantially. For example, in the case of the argon ion beam which carries out incidence at 3 degrees, typical particle energy is about 1 keV, and the typical total dose is abbreviation 10-18cm-2.

[0035] Drawing 2 shows another operation gestalt for cutting off the carbon nanotube array which aligned using the oxidizing atmosphere and the temperature gradient. The carbon of the solid-state of all forms burns under existence of a hot oxygen content ambient atmosphere, for example, essentially forms the gas of CO or CO2. the carbon nanotube edge burned and opened -- for example, P.M.Ajayan etc. -- "Opening

carbon nanotubes with oxygen and implications for filling" to depend -- Nature, Vol.362, and 522 (1993) It has been explained as shown. However, the reaction was performed about the nanotube which was suitable without control of extent of opening of the obtained nanotube, or die length at random.

[0036] Symmetrically, according to this invention, and some carbon nanotubes 20 which aligned were controlled by using a slide, a SUI ping, or low TETINGU actuation, for example, making the heated body like the hot blade (heated cutting edge) 22 contact, it is heated at a perimeter or low temperature by the predetermined approach. The heated body offers a temperature gradient. That is, they are an elevated temperature and temperature low in a lower part in the upper part of a nanotube 20. These parts of the nanotube 20 which reaches the critical temperature of about 400 degrees C or more react with oxygen, and stop for example, burning.

[0037] It depends for the critical temperature for nanotube combustion on the diameter of each bundle of each nanotube or a nanotube at the oxygen section partial pressure in an ambient atmosphere, and the contact time list between a hot blade and a carbon nanotube. Use of the hot blade 22 of the concentrated body with which a specific configuration or others sharpened reduces the range of combustion of the already cut-off nanotube. It is used in order that a spacer may maintain predetermined sweep height on the support substrate 24 desirably. For example, it is the rail of the fixed height of the pair arranged near the edge of a nanotube array sample. 1 time of the sweep of a blade 22 or several times of sweeps can be used.

[0038] Generally, the body heated can be formed from a metal or a ceramic ingredient, and is which suitable configuration. The body heated is heated by which suitable technique to desired temperature. For example, in order to use the ingredient electrically heated in order to heat the body like the cutting edge of the razor partially set in the flame of a torch in order to make desired temperature reach, for example, a high resistance heating element alloy, it is possible to place the body into a furnace. When the direction and strength of flame can control well, it is also possible to use the flame itself.

[0039] In this invention, such a frame is considered to be the body heated. The temperature at the tip of a blade in contact with a nanotube is at least 400 degrees C, and is at least 600 degrees C desirably. It is possible to use 100% of oxygen ambient atmosphere or a thin oxygen ambient atmosphere (for example, 5%O2 in air or Ar) depending on the desirable level of control and a desirable speed of cutoff. perfect --

again -- ** -- it is also possible to use the ambient atmosphere of a carbon dioxide partially. A control sample is easily used, in order to determine the suitable condition of cutoff of the nanotube by this operation gestalt.

[0040] In another operation gestalt, nanotube cutoff is performed by dissolving the carbon from a nanotube edge in the melted metal (drawing 3 A) or the melted solid-state metal (drawing 3 B). The comparatively high solubility in the inside of the predetermined liquid of carbon or a solid-state metal is known well. To the level of desired cutoff height, the growth edge of the nanotube 30 which aligned as shown in drawing 3 A is dipped in the melted carbon dissolution (namely, carbon fusibility) metal 32, is removed from molten metal and cooled.

[0041] In order to prevent oxidation of molten metal, a reaction is desirably performed in an inert atmosphere like Ar, or a reducing atmosphere like H2. When desirable, residual metal coating or the waste near the nanotube edge cut off is dissolved from an acid, and the cut-off beautiful tip is exposed. In use of the liquid fusibility for the nanotube cutoff in this invention, although a refractory metal like iron is also possible, the molten metal which has the high fusibility over a low-melt point point and carbon comparatively is used desirably.

[0042] For example, a rare earth metal like Ce (the liquid fusibility of the carbon in melting point =798 degree C and -900 degree C is -25 atom % carbon) and La (melting point = 918 degrees C) is useful. for example, Ce and 28 atoms % -- low melting alloys like Cu (melting point = 424 degrees C) or La, and 30 atom %nickel (melting point = 532 degrees C) are also usable. Other various alloys and the alloy which contains at least one rare earth metal and at least one non-rare earth metal like transition metals especially are also useful.

[0043] Unlike use of molten metal, drawing 3 B shows use of the solid phase diffusion dissolution of carbon. Specifically, the solid-state metal or alloy 40 which has carbon like Ce, La, La-nickel, and Fe or Mn and high solid-state fusibility is heated by the elevated temperature of 400 to 1000 degree C in inactive or a reducing atmosphere. And the nanotube 42 which aligned is desirably rubbed gently by repetitive sweep actuation to the thick solid-state metal 40 until the die length of a request of the edge of a carbon nanotube 42 dissolves by solid phase diffusion.

[0044] The actuation to grind may be linearity, rotation, or random actuation. Desirably, in order that at least one spacer 44 may control cutoff height, it is used between a nanotube 42 and the hot carbon fusibility metal 40. In this solid phase approach, at least 20 degrees C

of temperature of a carbon dissolution solid-state metal or an alloy are desirably maintained low from that melting point.

[0045] Another operation gestalt for cutting off the carbon nanotube which aligned is shown in drawing 4 A-4D. According to this operation gestalt, the carbon nanotube 50 which aligned is put in by the capsule substantially in the solid-state matrix 52 as shown in drawing 4 A and 4B. Capsulation is performed using which suitable matrix ingredient containing the polymer, the ceramic, or composite material containing a metal and epoxy.

[0046] For example, the molten metal or the alloy of low-melt point point solder permeates a nanotube array, and has it permitted to solidify. Desirably, such a metal or an alloy contains the small mixture of the carbide formation element (for example, Ti, V, Cr, Mn, Fe, Zr, Nb, Mo, Hf, Ta, W) for improving the wetting of a nanotube. Typically, there are not more atomic numbers of a carbide formation element than 50% of the number of the carbon atoms in a nanotube.

[0047] In order to make a nanotube array permeate, and to dry a composite and to return a metal salt to a metal matrix, it is also possible by burning a composite to put a nanotube into the water or the solvent which contains the binder of fusibility in water or a solvent arbitrarily at a capsule in metal salting in liquid like $CuCl_2$, $CuSO_4$, or $InCl_3$ of fusibility. The capsulation agent (conductivity or non-conductive) of a polymer is also useful.

[0048] It is cut or ground by a nanotube array substrate and parallel in order that the composite structure 54 containing the nanotube 50 which was embedded into the solid-state matrix 52 and which aligned may offer the cut-off nanotube 56 as shown in drawing 4 C. In the case of for example, a metal matrix, in the case of an acid, a base, water solubility, or a solvent fusibility matrix, the front face where this structure was cut or ground is lightly etched with water or a solvent. The processing step of this last makes the structure 60 of the request containing the ejection nanotube 58 which has the edge and the comparatively uniform height which were cut off.

[0049] The nanotube array structure which is formed of this invention and which was aligned and cut off is useful for various devices containing the microwave vacuum-pipe device, flat panel field emission display, and hydrogen storage device which are explained below.

[0050] The emitter structure including nanotube emitter structure formed as the device above-mentioned was carried out is useful for various devices containing a microwave vacuum-pipe device and a flat panel field emission device. Since sufficient electron emission in low applied

voltage is typically attained by existence of the acceleration (typically about 1 distance of -10 micrometer) gate electrode close to an emitter, in order to strengthen the capacity of structure, it is convenient to have many gate holes in emitter structure. Specifically, the gate structure of micron size of the fine scale which has many gate holes is advantageous in order to acquire high emission effectiveness.
[0051] Therefore, in 1 operation gestalt of this invention, a grid construction is formed ahead of the nanotube emitter structure shown here. A grid is a conductive element arranged between an electron emission cathode and an anode. Although it dissociates from the cathode, this is fully less than 10 micrometers at near and the tip of a nanotube which carries out electron emission typically at a nanotube emitter, in order to excite electron emission. This near spacing is possible only when it has height with a comparatively uniform emitter tip. As mentioned above, the manufacture process of this invention offers the nanotube tip which shows such homogeneity.
[0052] Generally the grid is separated from the cathode by electric insulating layer like oxidation aluminum or a silicon dioxide. The grid construction in this invention has many holes in a convenient thing, for example, contains a conductive layer in it at an electric target like a thin film or the thin foil. In each hole, when electric field are impressed between a cathode and a grid, many nanotubes emit an electron.
[0053] Typically, the dimension of a grid hole is the range of 0.05 to 100 micrometer in the average upper limit (for example, diameter), is at least 0.1 micrometers preferably, and in order that it may make manufacture easy, it is at least 0.2 micrometers preferably. The average upper limit is not larger than 5 micrometers, in order to reduce an electrical potential difference required since the consistency of a grid hole is increased and electron emission is produced large more more preferably [it is desirable and] than 20 micrometers. A circular hole is advantageous and these offer the desirable parallel electron beam which has a comparatively low perpendicular moment speed.
[0054] a grid -- the thickness of a conductor is in the range of 0.05 to 100 micrometer typically, and it is 0.05 to 10 micrometer preferably. Although grid conductor material is typically chosen from Cu, Cr, nickel, Nb, Mo, W, or a metal like these alloys, use of an oxide nitride and a conductive ceramic ingredient like carbide is also possible. Typically, the grid construction which was able to open the hole is prepared by the usual thin film volume and etching of a photolithography.
[0055] It is the high density hole vacancy gate structure where the grid was indicated by the convenient thing at U.S. Pat. No. 5,681,196 and No.

5,698,934. Especially the combination of very detailed and the nanotube emitter of high density, and high density gate hole structure is advantageous. Such high density gate hole structure is formed in convenience by using the particle mask of a micron or submicron size.
[0056] After formation of nanotube emitter structure, the upper limit is smaller than 5 micrometers, and, specifically, the mask particle of a desirable metal smaller than 1 micrometer, a ceramic, or a plastics particle is added to an emitter front face by the spray or sprinkler spraying. The dielectric film layer or glass like SiO2 accumulates on mask particle by vacuum evaporationo or sputtering.
[0057] A conductive layer like Cu or Cr deposits on a dielectric layer. The emitter region which is under each mask particle for the shadow effectiveness does not have a dielectric film. And brush removal is carried out simply, or mask particle is blown away, and the gate electrode which has the hole of high density is left behind. Drawing 5 shows such a particle mask technique.
[0058] The mask particle 70 is arranged on the projected nanotube emitter 71. The mask particle 70 blocks the part of the nanotube emitter 71 with deposition in the conductor 75 on the substrate 76 of an insulating layer 73 and the grid conductor layer 74. When the mask particle 70 is removed, a nanotube 71 is exposed through the hole obtained. The structure acquired can be included into a device.
[0059] Drawing 6 is the outline sectional view of the traveling wave tube (TWT) in a typical microwave vacuum-pipe device and here. A tubing device includes the microwave output window 84 where the microwave power pulled out from the interaction structure 83 and the electron with which the input window 82 for introducing the empty tubing 80, the electron source of the form of an electron gun 81, and a microwave input signal and an electron interact with an input signal is taken out from tubing.
[0060] After the focusing magnet and output microwave power which are not illustrated for other component parts to centralize an electron beam through the interaction structure 83 in the case of TWT are generated, the internal damping machine which is not illustrated for absorbing the collector 85 which collects electron beams, and the microwave power returned to tubing by reflecting from the inequality of an output is included. Typically, the interaction field 83 is [as opposed to / TWT / a broadband application] a conductive spiral, and is a joint cavity field to a high power application.
[0061] After an electron beam leaves a gun, an electron gun 81 is an electron source which generates an electron beam, and accelerates and is centralized, as a desirable orbit is flowed. Drawing 7 shows the usual

electron gun which consists of an aperture door node 93 for leading further the focusing electrode 92 and beam 94 for centralizing one or two grids 91 or more for carrying out induction of the electronic emission, and an electron on a beam to the interaction structure 83. Because of TWT application, a low battery and the thin long electron beam of high current density are comparatively advantageous. the pierced earring gun from the planar cathode with which the electron gun faced the planar anode, a cone two-poles electrode, and a concentric circle -- or the structure to a more elaborate design like a spherical-surface cap cathode is attained to. For example, A.W.Scott and supra Refer to.

[0062] In actuation of the device shown in drawing 6 and 7, an electron beam 94 is accelerated from a cathode 90 with the high voltage impressed to the grid 91 and the anode 93. And an electron beam is driven into the interaction structure 83 which interacts with a microwave input signal so that a beam 94 may be amplified as an electron and a signal may advance through [both] the interaction structure 83. An electron runs conveniently at the same rate as a microwave signal on the interaction structure 83. The power of an input signal modulates an electron beam 94, and the modulated electron beam 94 generates the form where the input signal was amplified by the output 84.

[0063] A cathode 90 and a grid 91 are the sources of the electron to the electron beam in TWT of drawing 6 . A cathode has the following properties and capacity conveniently. (1) The front face which can emit an electron is shown, without needing heating or external excitation like an impact. (2) Supply high current density. (3) It has the long life of operation continued without the ability of the electron emission weakening substantially. (4) Permit generation of the narrow beam accompanied by the small breadth in the electronic moment. (5) Permit generation of the modulated electron beam in a field or its near with a cathode.

[0064] The usual thermion cathode and the cold cathode containing the nanotube emitter projected symmetrically show these properties. When electric field are impressed, specifically, quick room temperature emission is possible for nanotube mold cold cathode. These permit generation of the electron beam modulated in the distance of several microns like the case of the beam modulation directly performed by the grid, enable use of the shortened interaction field, and bring about a more nearly lightweight and compacter device.

[0065] In a microwave vacuum-pipe device, when using nanotube mold cold cathode, it is desirable to maintain an electron beam to the breadth in rational level. From a cathode surface, an electron is the rate of non-

zero and appears at various include angles to a surface perpendicular. Therefore, the electron by which field emission was carried out has distribution of a moment value in the direction of an electron beam orbit. All the tolerance as a result of the electron orbit in the perpendicular moment which is not desirable, and a microscope scale reduces the engine performance of a microwave amplifier by increasing the minimum diameter which a shot noise and a convergent beam may reach to the pass from such effectiveness, i.e., random electron emission, and a cathode to an anode.

[0066] Therefore, when an electron beam is not almost parallel, it is desirable to forbid the electron beam from the hole with which it differs in a grid from uniting. When [which a beam unites] emitting according to an individual on the other hand, specifically, the phase space consistency of the beam as a result will fall. This is because an electron is discovered with various different moments also in which predetermined point.

[0067] By making an electrostatic lens in a hole, the angle of divergence from each hole can be reduced. However, the theorem of RYUVIRU restricts the range where a lens can reduce a perpendicular moment speed. A substantial improvement is not obtained when an emission field is equal to a lens hole. When an emission field is smaller than a lens hole, perpendicular moment distribution can be reduced by suitable lens design by the ratio of the radius of an emission field to the radius of a lens.

[0068] therefore, the small spot near the core of each hole -- that is, the thing of the area of a hole for which the emission only from at most 50% is permitted preferably is desirable 70% at most. a specific emission hole -- receiving -- a hole -- emission is controllable by patternizing a substrate so that only a small field smaller than a field is conductivity. For example, by carrying out the volume of the non-emitting upper layer on the nanotube emitter except the core of a hole, it is also possible by controlling a nanotube coalesce process to control emission so that only the central field in an emission hole may be activated and an electron may be emitted.

[0069] Multilayer aperture DOGURIRU is useful in order to decrease an angle of divergence. In such a multilayer grid, the 1st grid operates with electronegative potential. the 1st grid -- the average maximum hole dimension (in for example, the case of a circular hole diameter) -- it is on 0.05 thru/or a 10 time cathode typically, and they are 0.3 thru/or twice preferably. Typically, the hole is circular, has 0.05 thru/or the diameter of 100 micrometers, is at least 0.1 micrometers preferably, and

is at least 0.2 micrometers more preferably.

[0070] This 1st grid reduces the electric field in the cathode front face near the edge of a hole, and, thereby, controls the emission from an edge preferentially. Typically, a consecutive grid shows a forward electrical potential difference to a cathode. a multilayer grid construction has two-layer at least, and is preferably shown in drawing 9 -- as -- the grid of at least four layers -- it has a conductor. a grid -- it is separated by Insulators 101A, 101B, 101C, and 101D, and Conductors 100A, 100B, 100C, and 100D define the hole 102 which aligned.

[0071] the cathode with which the nanotube emitter 103 arranged in each hole 102 has been arranged on a substrate 105 -- it is supported with the conductor 104. a grid -- a conductor -- 100A-100D makes it possible to be concentrated while an electron beam advances. Generally, bias of the 1st grid layer nearest to an emitter (100A) is carried out to negative, and it reduces the perpendicular moment by control of the field emission near the edge of the grid hole 102.

[0072] The negative bias on the 1st grid centralizes the electron beam which emits to what has the moment more near parallel to a surface perpendicular. When large enough for forcing emission also when there is existence of the grid by which the electric charge of the electric field impressed to an anode was carried out to negative, a single grid offers a useful property similarly. However, two or more grids are advantageous to reducing the required electrical potential difference on an anode, and advantageous to offering the electron beam equilibrated more by fitness.

[0073] A multilayer grid construction is formed of the usual thin film deposition and phot lithography technique. The grid construction of drawing 8 can also be formed by the particle mask technique mentioned above as shown in drawing 9 and 10. Typically, the thickness of grid conductor-layer 100A-100D is in 0.05 thru/or the range of 100 micrometers, and is in 0.1 thru/or the range of 10 micrometers preferably. Although a grid conductor layer is generally chosen from metals like Cu, Cr, nickel, Nb, Mo, and W, or these alloys, use of oxide, a nitride, and a conductive ceramic like carbide is also possible. Insulator layer 101A-101D is typically formed from a silica or an ingredient like glass.

[0074] In drawing 9 , the mask particle 106 is felloe magnetism (for example, Fe, nickel, Co(es), or these alloys) typically. Desirable particle size is the range of 0.1 to 20 micrometer in an average diameter typically. For example, a vertical field is impressed in arrangement of the particle by sprinkler spraying of a up to [nanotube

emitter structure]. This makes the chain of a long ball form in perpendicularly at least two particle is contained in the ferromagnetism particle 106.

[0075] Although the chain of some balls may have nearby particle many from other things, this does not affect the process on which a multilayer grid construction is made to deposit. the insulating spacer film (101A-101D) to a multilayer stack, and a grid -- a conductor -- pulling magnetically after membranous (100A-100D) alternation-deposition using a permanent magnet -- or the ferromagnetism particle 106 is removed by chemical etching.

[0076] Alternative particle mask approach is roughly shown in drawing 10 . In this alternative-like approach, it was extended, i.e., the ferromagnetism particle 107 of ** length is sprinkled under existence of a perpendicular field so that it may work as mask particle during deposition of the multilayer grid construction (100A-100D and 101A-101D) to the substrate 105, conductor layer 104, and nanotube emitter 103 top and they may stand up perpendicularly. And a particle mask is removed as mentioned above.

[0077] Typically, the extended mask particle 107 has the average shaft upper limit of the range of 0.1 to 20 micrometer, for example, a diameter. For example, it is possible to form particle 107 through the hole vacancy template which has been arranged at the height of the request on a nanotube emitter and which is not illustrated by thin film deposition (for example, sputtering, vacuum evaporationo, non-electric-field plating) of a mask ingredient.

[0078] The suitable ingredient for the extended mask particle 107 contains a metal like Cu, aluminum, and nickel, the polymer (for example, polyvinyl acetate, polyvinyl alcohol, polyacrylamide, acrylic nitril-styrene butadiene rubber, or ABS) which melts into water or a solvent easily, an volatile polymer (for example, PMMA), or the salt (for example, NaCl) which dissolves easily. After deposition of particle, a template is removed and a multilayer grid construction is formed.

[0079] The cathode and gate structure of drawing 8 do not necessarily have the flat shape of surface type, when used in a microwave amplifier. The curve substrate which the thin film array emitter deposited the remolded bulk nanotube composite emitter or on it can be used. In the case of an ingredient like Si, in the case of etching, mechanical polish, Cu, Mo, Nb, W, Fe and nickel, or a ductility metal like these alloys, a curve substrate is formed of plasticity deformation.

[0080] The nanotube content cathode and multilayer grid construction of drawing 8 are used for a convenient thing in TWT instead of a thermionic

emission cathode. Moreover, the cathode/grid construction of drawing 8 are curving slightly conveniently in order to centralize the emitted electron on one beam.

[0081] The nanotube emitter structure of drawing 8 reduces the perpendicular moment speed of the electron emitted from a cathode according to four descriptions. (1) Low-battery emission is desirable in order to reduce beam divergence. When emitter geometry is kept constant, perpendicular moment speed is the square root of an emission electrical potential difference. Use of the projected nanotube emitter enables low-battery emission, and reduces the perpendicular moment in microwave amplifier actuation. (2) Electron emission is restricted to the central field part smaller than the whole grid hole area for whether your being Haruka. (3) Centralize an electron beam by the stack of a multilayer grid construction. (4) A curve substrate centralizes an electron beam further.

[0082] In order to manufacture a flat panel field emission display, the nanotube mold emitter of this invention can also be used. Such a field emission display consists of for example, a bipolar mold (namely, cathode-anode configuration) or a trilateral mold (namely, cathode-shot-anode configuration). Desirably, a grid construction is used. More desirably, as mentioned above, high density hole gate structure is arranged near the nanotube emitter cathode.

[0083] Because of a display application, in order to divide, to equalize the emission characteristic and to guarantee the homogeneity of display quality, as for the emitter ingredient in each pixel of a display (cold cathode), consisting of two or more emitters is desirable. For the detailed property of a carbon nanotube, an emitter offers many emitting points. It is diameter (10 thru/or 100nm) of a capillary typically, and when 50% of nanotube consistency is assumed, it is an emission tip with more 100x100 micrometer than 104 per pixel of 2.

[0084] The emitter consistency in this invention is 1/micrometer2 at least, and is 10/micrometer2 at least more desirably. Typically, since it is attained by existence of the acceleration gate electrode which approached (typically distance of about 1 micron), in order to use the capacity of two or more emitters, as for the efficient electron emission in low applied voltage, it is useful to have two or more gate holes in a predetermined emitter region. In order to increase emission effectiveness, it is also desirable to have the structure of a fine scale and micro size of having as many gate holes as possible.

[0085] Drawing 11 shows the flat panel field emission display which used the nanotube emitter structure of this invention. This display contains

the anode 114 which set spacing and has been arranged from the emitter 112 in the cathode 110 containing two or more nanotube emitters 112, and a vacuum well-closed container. the anode formed on the transparent insulating substrate 118 -- a conductor 116 is offered with the fluorescent substance layer 120, and is attached on the support column which is not illustrated. An emitter is approached, and between a cathode and an anode, the hole vacancy conductivity gate layer 122 sets spacing, and is arranged between. Conveniently, the gate 122 sets spacing from a cathode 111 by the insulator layer 124, and is arranged.

[0086] An airtight is maintained, vacuum suction of the space between an anode and an emitter is carried out, and an electrical potential difference is impressed according to a power source 126. the electron by which field emission was carried out from the nanotube emitter 112 is accelerated with the gate electrode 122 -- having -- transparence like an indium and a stannic-acid ghost -- it moves toward the anode conductor layer 116 which is a conductor. A display image is generated when the accelerated electron is equivalent to the fluorescent substance layer 120.

[0087] It is also possible to use the nanotube structure where this invention was cut off for an energy are recording device like a light weight and a high energy consistency dc-battery. It is known that the hole with a detailed molecular dimension can suck up for example, absorb a lot of gas. For example, the carbon nanotube in which the edge carried out opening sucks up many hydrogen 3 times rather than the new (as grew) nanotube which has the edge which the cap attached.

[0088] for example, A.C.Dillon etc. -- "Storage of hydrogen in single-walled carbon nanotubes" to depend -- Nature, Vol.386, and 377 (1997) Refer to. Sucking of the improved hydrogen is desirable for an energy are recording application like the efficient fuel cell for an electric vehicle. The nanotube edge which the big consistency which is opening to coincidence the nanotube structure of high density homogeneity height where this invention was cut off, for hydrogen adsorption, therefore offers the useful property for hydrogen are recording opened is offered.

[0089] Similarly, the cut-off nanotube structure is suitable for comparatively easy sucking of a dissolved alkali metal like the lithium which tends to form a graphite intercalation compound, sodium, POTAJIUMU, and caesium. Electrolysis-are recording of the lithium ion in the inside of a graphite type ingredient is reversible as known as a lithium ion battery.

[0090] J.R. Dahn etc. -- "Mechanisms for Lithium Insertion in Carbonaceous Materials" to depend -- Science, Vol.270, and 590 (1995)

Refer to. Therefore, the nanotube structure where this invention was cut off can be used as an efficient negative electrode in a secondary (it can charge) cell like a lithium ion battery. Especially the low consistency of a carbon nanotube will offer the high energy consistency per unit cell weight.

[0091]

[Effect of the Invention] As explained above, this invention can offer the approach of improving the radiation property of the ensemble of the nanotube which aligned.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing showing cutoff of the nanotube by 1 operation gestalt of this invention which aligned.

[Drawing 2] Drawing showing cutoff of the nanotube by another operation gestalt of this invention which aligned.

[Drawing 3] Drawing showing cutoff of the nanotube by the further operation gestalt of this invention which aligned.

[Drawing 4] Drawing showing cutoff of the nanotube by the additional operation gestalt of this invention which aligned.

[Drawing 5] Drawing showing the nanotube cathode formed of this invention.

[Drawing 6] Drawing showing traveling-wave-tube structure.

[Drawing 7] The enlarged drawing of the electron gun structure of the traveling wave tube of drawing 6 .

[Drawing 8] Drawing showing the many grid constructions designed in order for this invention to extract an electron beam from a nanotube cathode front face, and to accelerate and to make it concentrate.

[Drawing 9] Drawing showing the formation of a multilayer grid construction which carries out magnetic mask particle stack use.

[Drawing 10] Drawing showing formation of the multilayer GURI@DDO structure which uses the extended mask particle.

[Drawing 11] Drawing showing the flat panel field emission display by this invention.

[Description of Notations]

10 High Energy Beam

12, 30, 50 Nanotube which aligned

14 Waste
20 Carbon Nanotube Which Aligned
22 Hot Blade
24 Substrate
32 Carbon Fusibility Metal
40 Solid-state Metal or Alloy
42 Nanotube
44 Spacer
52 Solid-state Matrix
56 Cut-Off Nanotube
58 Projecting Nanotube